DOLOMITES

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ABSTRACT

The origin of dolomite is a subject of much interest in Ohio as this state is underlain by great thicknesses of such rock, some of high purity. Within the last few years over 335 detailed analyses have been made. These analyses have been reduced by calculation to their mineral components, which treatment throws much light on the nature of the rocks and reveals certain inferences concerning the origin of both dolomite and limestone. From these studies dolomite was deposited in sea water with normal salinity and limestone in that diluted by fresh water from the land areas.

CONTENTS

INTRODUCTION

The groundwork for the following paper is as follows:

(a) The examination of a thick section of carbonate rocks in Ohio, Cambrian to Permian time.

(b) Much detailed work in identifying, sectioning and sampling the deposits.

(c) Careful appraisal of mineral components of over 400 high-grade chemical analyses of dolomites and limestones throughout the section.

(d) Use of some of the common chemical reactions involving carbonates.

(e) The aid of a few of the simple laws of thermo-chemistry.

(f) The chemistry of fresh and salt water as defined by Clark.

(g) The fact that the ocean is the only source for such a large supply of magnesium oxide, MgO, or rather atomic magnesium, Mg, in an active form as shown by Clark.

Some of the generalizations considered are as follows: Dolomites are the normal and most abundant deposits of carbonate rocks laid down in the ocean throughout the geological ages. In the limestones this compound, $CaMg(CO_3)_2$, also bears a rather conspicuous part. Many dolomites approach chemical purity, that is, they contain no or little limestone. Conversely the limestones are always more or less dolomitic in character. A detailed physical and chemical study of such rocks in Ohio[1] indicates that the dolomites are primary in origin, that is, they were deposited as found today. No alterations are apparent except very locally and

[1]See Bull. 42, Geological Survey of Ohio, also records in files.

then the change is more physical than chemical. Dolomites originated through chemical activity in sea water of normal concentration, either in shallow or deep water but largely under the former condition.

On the other hand, limestones, the less abundant carbonate rocks of the ocean, were deposited under marine conditions but where the normal salt solutions were somewhat diluted through the influx of fresh water from land sources. Thus limestones carrying a high content of calcium carbonate are usually in association with shale deposits, either above or below or within the formation. In general the shale materials originated on the land and were carried to the ocean by streams. The streams not only diluted the sea water but brought in large supplies of carbonic acid, CO_2 or H_2CO_3 and some soluble calcium bicarbonate salt, $Ca(HCO_3)_2$. In the great carbonate formations of the Mississippian, Devonian, Silurian, and Ordovician systems the limestone deposits are, with few exceptions, placed between shales. Further, the basal portion of such limestones, if thick, is much higher in dolomitic matter than the upper portion. In the Pennsylvanian and Permian systems in Ohio the carbonate strata of fresh water origin[2] and also those of marine derivation[3] are limestones with a low content of dolomites, $CaMg(CO_3)_2$. The fresh water limestones occur under, and the marine limestones over the coal beds which are known to have been deposited on land through humid conditions. Clays, shales, and sandstones are found as associate deposits. Such limestones, in the coal formations, are usually thin but widely spread in distribution.[4]

CHEMICAL NATURE OF CARBONATES

The carbonate rocks are built around the carbon atom, C, as the nucleus of the acid component. Through oxidation this carbon, C, changes to the oxide form, carbon monoxide, CO, or the dioxide, CO_2, most commonly the latter. Then through hydration, or the addition of water, carbon dioxide, CO_2, produces the unstable acid, H_2CO_3, and the acid salts of $H_2(HCO_3)_2$, as $Ca(HCO_3)_2$, $Fe(HCO_3)_2$, $Mg(HCO_3)_2$, $Mn(HCO_3)_2$, all soluble substances and carried in fresh waters. The changes may be given as follows:

$$\begin{array}{l} C \\ \downarrow \\ C + O_2 = CO_2 \\ \qquad\quad \downarrow \\ \qquad\quad CO_2 + H_2O = H_2CO_3 \text{ or } H_2(HCO_3)_2 \end{array}$$

Carbon is one of the original elements and in some form is widely distributed in nature. In this discussion carbon dioxide, CO_2, is the compound of most interest. At present, and in the past, most of the carbon dioxide in the air and in solution in fresh or saline waters is derived directly or indirectly from the decay or from the exhalation of organic matter, animal or vegetable, on the land surface, in fresh water or in the ocean. Those of most concern are the parts held in solution in both the fresh waters of the land areas and in the saline waters of the sea. Thus all the streams are pouring continuous supplies of carbon dioxide in some form into the ocean and the sea with the changing of its myriad organic forms, through life

[2]The fresh water limestones include the Salem, Lower Freeport, Upper Freeport, Mahoning, Bloomfield, Ewing, Elk Lick, Clarksburg, Summerfield, Pittsburgh, Redstone, Fishpot, Benwood, Arnoldsburg, Uniontown, Waynesburg, Elm Grove, Lower Washington, Middle Washington, Upper Washington, Nineveh and Gilmore members.

[3]The marine strata include Lowellville, Boggs, Lower Mercer, Upper Mercer, Putnam Hill, Zaleski, Vanport, Hamden, Brush Creek, Cambridge, Portersville, Ames, Gaysport and Skelley members.

[4]For the relations of coal, clay, fresh water and marine limestones, see Bull. 26, Fourth Series, Geological Survey of Ohio, pages 533–568.

and death, generates large amounts for chemical activity. In such ways carbon dioxide has been produced in greater or lesser quantities throughout the geological ages since life began, even in its most simple forms. Hence organic life appears to supply the needed quantity of carbon dioxide to complete the reactions for the precipitation of dolomites and limestones.

SOURCE OF COMPONENTS

The basic components, MgO or CaO or Mg and Ca, were supplied by the ocean with some augmentation from the land areas. Sea water even after the extraction of large quantities of magnesium for the formation of dolomites throughout the geological ages is still rich in that substance. According to Clarke[5] the salinity of the ocean varies from 3.301 to 3.737 per cent and the mean of seventy-seven analyses is as follows:

Cl	55.292
Br	.188
SO_4	7.692
CO_3	.207
Na	30.593
K	1.106
Ca	1.197
Mg	3.725
Total	100.000

Thus the quantity of magnesium is over 3.11 times that of the calcium and the reacting value of the former is 5.13 times that of the latter. Hence in any reaction in normal sea water, involving precipitation, magnesium will be the dominating component and dolomite and not limestone will be the resulting product.

Clarke states:[6] "In chemical character, fresh and salt waters are opposites, as a brief inspection of the data will show. In ocean water, $Cl > SO_4 > CO_3$; in average river water, $CO_3 > SO_4 > Cl$. So also for the bases—in the first case, $Na > Mg > Ca$; in the other, $Ca > Mg > Na$—a complete reversal of the order."

Commonly in nature the reaction that takes place in precipitation is the one involving the least exchange of heat or of energy used. The heats of formation of calcium carbonate and magnesium carbonate in the simple reactions, per unit of compound are as follows:[7]

Calcium carbonate, $CaO \cdot CO_2$	451 calories
Magnesium carbonate, $MgO \cdot CO_2$	349 calories

Then under such conditions with a preponderance of magnesium in the ocean waters, with a higher reacting value for the element, magnesium, with less heat exchange, and with less solubility in the salt solution, the precipitated compound, thus leaving the field of chemical activity, should be dolomite and not limestone. Here magnesium oxide, MgO, is the dominating base in such a solution and when this is allowed to react with the carbonic acid, $H_2(HCO_3)_2$ or the acid salt, $Ca(HCO_3)_2$, brought in from the land surface, the resulting product is dolomite. In fresh water, limestone and not dolomite would be the favored precipitate as the acid H_2CO_3 or $H_2(HCO_3)_2$ is abundant and as the base CaO is much in excess of MgO. The resulting products are those of simple precipitation.

In the waters from land areas both the acid and basic components are much different from those of marine waters and consequently the chemical activity of the former will be unlike in some respects from that of the latter. As an example

[5]Clarke, Frank Wigglesworth, Data of Geochemistry, Bull. 330, U. S. G. S., pages 94–95.

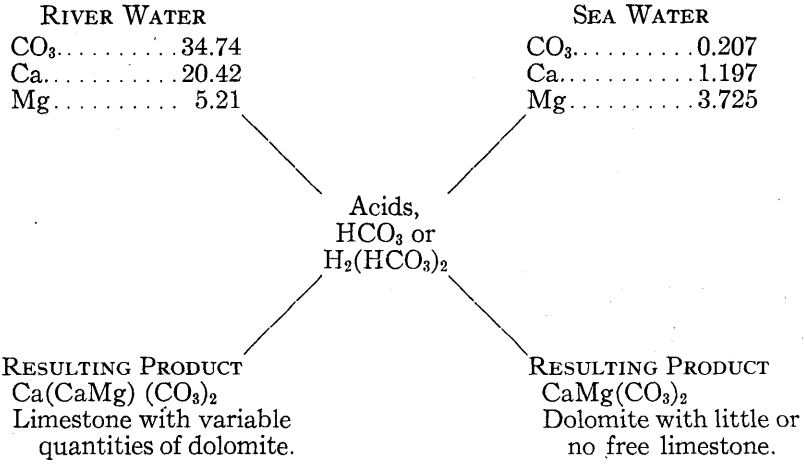
[6]Clarke, Frank Wigglesworth, Data of Geochemistry, Bull. 330, U. S. G. S., page 107.

[7]Richards, Joseph W., Metallurgical Calculations, Part 1, page 2020.

of surface water from the land areas that from the Mississippi River may be taken as representative.[8]

CO_3	34.74
SO_4	14.90
Cl	6.23
NO_3	1.57
Ca	20.42
Mg	5.21
Na	4.92
K	4.65
SiO_2	6.77
Al_2O_3	0.44
Fe_2O_3	.015

In this analysis of river water the Ca is 3.92 times the Mg which is far different from the proportions found in sea water. The content of CO_3 is also high; 34.74 for river water compared to 0.207 for sea water. Further it carries SiO_2, Al_2O_3 and Fe_2O_3 as soluble components. The direct comparison is as follows:



In fresh water the resulting product is a limestone with an appreciable but variable quantity of dolomite. Thus the reaction is not complete, yielding pure $CaCO_3$ or $CaCa(CO_3)_2$. However, in sea water, in the large majority of cases, the reaction reaches completion yielding $CaMg(CO_3)_2$, dolomite, with no free limestone and with the true chemical ratio. Under varying conditions mixtures of the two are common.

If dolomite is secondary, that is, first deposited as a limestone then changed to dolomite, much additional work would be involved in the reaction. This requires the solution of the originally precipitated limestone before the exchange of Mg for Ca could take place. Also other reactions would be involved in the adjustment. Such work would be done in a salt solution in which the Mg much exceeds the Ca and in which dolomite is evidently much less soluble than limestone as shown by the solution and disappearance of the shells of fossils in the dolomites, leaving only casts in the rock. The formation of dolomite in sea water is quite simple as "the monovalent ion HCO_3' is formed by preference, and to this some of the characteristic properties of the carbonates are due."[9] Some of these may be represented as follows: HCO_3', monovalent hydrocarbon ion; $Ca(HCO_3)_2$, soluble calcium bicarbonate and $CaMg(CO_3)_2$ dolomite.

[8]Clarke, Frank Wigglesworth, The Data of Geochemistry, Bull. 330, U. S. G. S., page 65.

[9]Oswald, Wilhelm, The Principals of Inorganic Chemistry, 1908, page 395.

DATA FROM OHIO

Let us see how this works out in the carbonate rocks of the past geological ages. In Ohio about 335 detailed analyses have been made of the dolomites and limestones in the Permian, Pennsylvanian, Mississippian, Devonian, Silurian and Upper Ordovician systems.[10] Further, some work but in less detail has been done on the rocks of the lower Ordovician and of the Cambrian systems. These analyses were computed to their mineral components, dolomite, $CaMg(CO_3)_2$; limestone, $CaCO_3$; and various other substances. These results are shown on page 224.

FRESHWATER LIMESTONES OF PENNSYLVANIAN AND PERMIAN SYSTEMS

In the coal formations, fresh water limestones make their appearance just under the Middle Kittanning coal of the Allegheny series of the Pennsylvanian system. From this place to the Duquesne coal, about the middle of the Conemaugh series, fresh water limestones are common below the coal beds and marine limestones above them. Above the Skelley limestone, or through the upper part of the Conemaugh series, through the Monongahela series of the Pennsylvanian system and then through the Washington and Greene series of the Permian system, all limestones present, and other strata also, are of fresh water origin. No marine influence is evident. Such strata are limestones in the sense that the dominating component in all cases is calcium carbonate, $CaCO_3$. However, dolomite, $CaMg(CO_3)_2$, is a constant component. In 18 analyses of five members, (Washington, Benwood, Fishpot, Redstone, Summerfield), the most prominent and best developed, the variation is from 3.44 to 24.77 per cent dolomite and the average content 18.01 per cent. The limestone component, $CaCO_3$, varies from 59.13 to 88.63 per cent and the shale and other incidental components from 5.49 to 22.39 per cent. Thus in the freshwater limestone formations the bases occur, as stated by Clarke, in the order $CaO > MgO$, followed by small amounts of K_2O, FeO, Na_2O, and MnO. The acid component, CO_2 or HCO_3', is dominant, with small additions of S_2, SO_4. and P_2O_5. In a way these formations may be considered types for strictly freshwater formations.

MARINE LIMESTONES OF THE PENNSYLVANIAN SYSTEM

In Ohio in the Pottsville, Allegheny and lower Conemaugh series of the Pennsylvanian system a number of marine limestones are present. These vary from a few inches to 20 feet or more in thickness but range commonly between 1 and 8 feet. Marine limestones, if present, occur directly or closely above the coal beds. This is true also of the fossiliferous shales of marine or brackish water origin. Throughout the Pottsville, Allegheny and lower Conemaugh series this repetition of marine or brackish water deposits above the coal beds occurs in 21 out of a total of 31 coals. The coal beds are of land origin as are also the underlying coal formation clays. Further, some of the shales and sandstones are thus derived. The marine limestones and fossiliferous shales were deposited when subsidence first carried down the carbonaceous land surface, on which had developed the clays and the coals, to such a level that inundation by sea water took place. They were thus laid down in shallow, relatively quiet and silt free waters at the close of the coal forming stages. Under such conditions the marine waters were certainly more or less diluted with fresh water as on the average the coal beds are repeated about every 21 feet in the column. The marine waters also had excellent opportunities for charges of carbonic acid, HCO_3', or $H_2(CO_3)_2$. Six of such limestone members

[10]Geological Survey of Ohio, Bull. 42, Dolomites and Limestones of Western Ohio and unpublished analyses of limestones in eastern Ohio.

FRESHWATER LIMESTONES

Name of Formation	Average Thickness in Feet	Number of Samples	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Argillaceous Siliceous and Other Impurities
PERMIAN SYSTEM					
Washington	9	1	3.44	88.63	7.93
PENNSYLVANIAN SYSTEM					
Benwood	37	2	9.99	76.04	13.97
Fishpot	32	10	24.77	59.13	16.10
Redstone	13	2	15.33	62.28	22.39
Summerfield	12	3	7.46	87.05	5.49

MARINE LIMESTONES

PENNSYLVANIAN SYSTEM					
Ames	1½	5	3.40	86.22	10.38
Cambridge	4	3	3.19	58.12	38.69
Brush Creek	20	2	3.80	33.04	63.16
Vanport	6	7	2.61	90.59	6.80
Putnam Hill	4	16	4.49	88.72	6.79
Lower Mercer	2	5	4.64	86.77	8.59
MISSISSIPPIAN SYSTEM					
Maxville	20	5	19.83	70.38	9.79
DEVONIAN SYSTEM					
Delaware	45	12	30.46	55.81	13.73
Columbus —top	50	20	29.00	67.96	3.04
—bottom	40	24	84.72	11.69	3.59
Lucas	50	6	86.30	9.50	4.20
Amherstburg	15	1	83.23	14.23	2.54
SILURIAN SYSTEM					
Monroe	570	85	93.90	2.34	3.76
Guelph-Cedarville	170	64	98.02	0.20	1.78
Springfield-West Union	20	21	84.40	3.13	12.47
Euphemia	6	3	96.55	0.76	2.69
Laurel	6	3	78.78	12.85	8.37
Dayton	8	5	70.01	17.20	12.79
Brassfield	27	17	22.29	72.23	5.48
Elkhorn	63	1	25.10	1.75	73.15
ORDOVICIAN SYSTEM					
Upper Part					
Richmond	265	1	10.69	66.47	22.84
Maysville	205	4	4.33	47.89	47.78
Eden	245	2	7.88	45.05	47.07
Utica	170	2	13.22	23.60	63.18
Trenton	185	1	12.57	74.84	12.59
Black River	425	2	14.14	79.83	6.03
Glenwood	10	1	22.99	4.04	72.97
ORDOVICIAN SYSTEM[11]					
Lower Part					
LOWER MAGNESIAN[12]	450	24	95.00	1.00	4.00
CAMBRIAN SYSTEM[13]	715	52	54.49	0.81	44.70

[11]Partial analyses and microscopic work show dolomite with high purity.

[12]Partial analyses and microscopic work show dolomite with high purity.

[13]Partial analyses and microscopic work show dolomite with fair purity, cut by many sandstone strata.

Crystalline rocks, mainly gneiss.

(Ames, Cambridge Brush Creek, Vanport, Putnam Hill, Lower Mercer) were sampled, 38 tests in all being made. In these the dolomite component $CaMg(CO_3)_2$, is quite low, varying from 2.61 to 4.49 per cent and averaging 3.89 per cent. The deposits are thus rich in limestone, CaCO, the common range being between 50 and 90 per cent. Further, they are variable but generally low in argillaceous, siliceous and other impurities. Hence they conform to deposition in diluted marine waters where the acid, HCO_3', or $H_2(HCO_3)_2$, was abundant and the bases largely supplied directly or indirectly from land sources.

MAXVILLE FORMATION

The Maxville formation of the Mississippian system is patchy in development in Ohio. Thus the deposits are broken, more or less scattered and variable in thickness. A break or unconformity is present both at the top and at the bottom of the formation. The thickness varies from 1 to 140 feet or more. It is of marine origin as shown by the fossils which, however, are not abundant and are confined largely to the shaly partings along the bedding planes. In general this limestone is finely crystalline, dense and hard. The underlying formations, 300 to 600 feet or more in thickness, are the shales, sandstones and conglomerates, all of marine origin but chiefly of land derived materials. In Ohio the upper, much worn and eroded surface of the Maxville formations is in contact with the Pottsville rocks of the Pennsylvanian system. The lost interval here represents the Mauch Chunk of the Appalachian Mountains area. In Ohio, where thick, the upper part of the Maxville formation is a limestone rich in calcium carbonate, $CaCO_3$, low in dolomite, $MgCO_3 \cdot CaCO_3$, and generally low in the common impurities. This part is used in the manufacture of Portland cement. However, the lower portion is quite dolomitic in character, being classed as a limey dolomite. In five samples, from top to bottom, the range of components is, dolomite, $CaMg(CO_3)_2$, 1.84 to to 72.81 per cent and limestone, $CaCO_3$, 4.18 to 95.25. The respective averages are 19.83 per cent for the former and 70.38 per cent for the latter. The lower portion thus shows the influence of marine conditions not far from land areas and the upper portion bears more toward shallow marine conditions in advance of the coal formation stages.

DELAWARE FORMATION

The Delaware formation in Ohio varies from 30 to 70 feet in thickness but averages close to 45 feet. It is a limestone, dark gray to dark with carbonaceous pigments, rather dense in character, often flinty and commonly rich in marine fossils. It is overlain directly by the Olentangy shale and this in turn by the Ohio shale rich in organic matter. The total shale covering is thus several hundred feet of land derived materials. The Delaware formation is underlain locally by the Marcellus shale, much like the Ohio in character, that is, black and carbonaceous but otherwise of land derived materials. Along much of the outcrop the Delaware lies unconformably on the Columbus formation. From 12 analyses, spaced over a wide area the Delaware should be classed as a dolomitic limestone of only moderate purity. On the average the dolomite component, $CaMg(CO_3)_2$, is 30.46 per cent, the limestone component, $CaCO_3$, is 55.81 per cent and the siliceous, argillaceous and other ingredients are 13.73 per cent. In these analyses the minimum and maximum figures are, dolomite, $CaMg(CO_3)_2$, 14.21 and 52.83 per cent and the limestone, $CaCO_3$, 35.73 and 78.16. The composition thus indicates that the formation was laid down in sea water somewhat diluted by fresh water which was rich in the acid, HCO_3' and contained bases in the proportion of $CaO > MgO$.

COLUMBUS FORMATION, UPPER PART

The upper part of the Columbus formation, from 50 to 60 feet in thickness, and made up of the Klondyke and Coral members in central Ohio and the Venice and Marblehead in northern Ohio, is consistently a limestone, light to light gray in color, rich in fossils and earthy to dense crystalline in texture. It is overlain by the Marcellus black shale or by the disconformity marking the stratum. On the other hand the basal portion of the Columbus formation is a dolomite with a small content of limestone, $CaCO_3$. Wherever tested the upper portion shows a distinct gradation downward in the content of $MgCO_3$. For example at Columbus the figures are:

	Thickness	$MgCO_3$	$CaCO_3$
	ft. *in.*		
Sample 241, top	14 3	5.19	91.99
242	11 3	10.90	86.76
243	16 6	12.88	84.98

At the O'Shaughnessy Dam in Delaware County the results are:

	Thickness	$MgCO_3$	$CaCO_3$
	ft. *in.*		
Sample 209 Klondyke, top member	22 0	7.32	90.13
207 Coral	23 7	11.31	86.33
206 Eversole	10 1	28.44	61.08
208 Bellepoint	14 4	39.90	58.04

In general the upper part of the Columbus formation must be classed as a limestone, always somewhat dolomitic in character and rather low in the common impurities. In 20 samples taken across Ohio the dolomite component, $CaMg(CO_3)_2$, varies from 9.23 to 66.91 per cent and averages 29.00 per cent. The limestone component, $CaCO_3$, runs as low as 26.88 per cent and as high as 89.75 per cent. The common impurities average about 3.04 per cent. Thus the data would indicate that the upper portion of the Columbus formation was laid down in marine waters, slightly diluted with fresh water bearing little sediments.

COLUMBUS FORMATION, LOWER PORTION

The lower portion of the Columbus formation, 20 to 50 feet in thickness, imparts a different story as far as origin is concerned. It is usually slight brownish gray to light brown in color, definitely crystalline in texture, impoverished in fossils, then only casts, and locally impregnated with chert. It is directly overlain, with only a bedding plane for parting, by the upper portion of the Columbus formation and underlain by formations of the Detroit River group or by the disconformity marking the absence of a thick section of such rocks. Rather commonly the Columbus formation rests on the Monroe dolomite. Little or no land derived sediments are found within basal Columbus rocks or are found associated in the older formations. They are marine in origin with little influence from fresh water changes. From 24 samples gathered over a wide area in western Ohio and representative of the formation the dolomite component, $CaMg(CO_3)_2$, varies from 44.17 to 97.27 per cent and averages 84.72 per cent. On the other hand the free limestone, $CaCO_3$, varies from 0.00 to 53.72 per cent and averages only 11.69 per cent. The two carbonates make up all but 3.59 per cent of the total. Such rocks were laid down by precipitation in sea water closely normal in concentration.

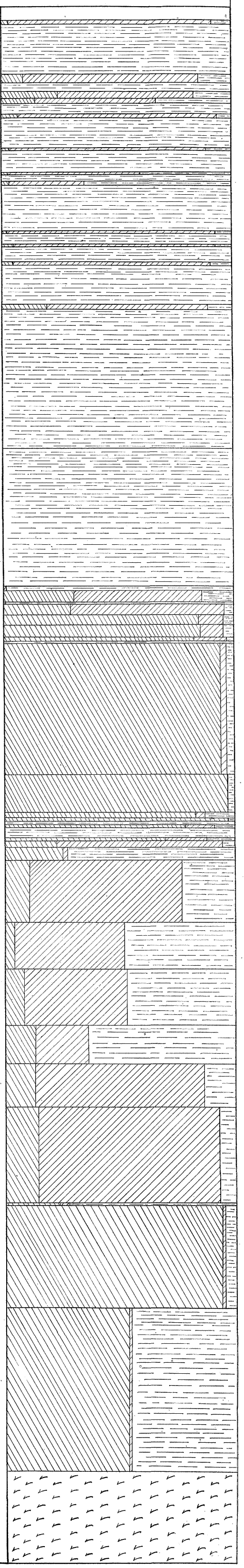
OHIO SECTION TO SCALE WITH COMPOSITION

FORMATION	MATERIAL	THICKNESS FEET	NO. OF SAMPLES	DOLOMITE $CaMg(CO_3)_2$	LIMESTONE $CaCO_3$	IMPURITIES
PERMIAN SYSTEM						
WASHINGTON	FRESH WATER IM.	9	1	3.44	88.63	7.93
PENNSYLVANIAN SYSTEM		227				
BENWOOD	FRESH WATER IM.	37	2	9.99	76.04	13.97
		45				
FISHPOT	FRESH WATER IM.	32	10	24.72	59.13	16.10
REDSTONE	FRESH WATER IM.	15	2	15.35	62.28	32.39
		57				
SUMMERFIELD	FRESH WATER IM.	12	3	7.46	87.05	5.49
		140				
AMES	MARINE IM.	2	5	3.40	86.22	10.38
		95				
CAMBRIDGE	MARINE IM.	4	3	3.19	58.12	38.69
		29				
BRUSH CREEK	MARINE IM.	20	2	3.80	33.04	63.16
		204				
VANPORT	MARINE IM.	6	7	2.61	90.59	6.80
		53				
PUTNAM HILL	MARINE IM.	4	16	4.49	88.72	6.79
		80				
LOWER MERCER	MARINE IM.	2	5	4.64	86.77	8.59
MISSISSIPPIAN SYSTEM		175				
MAXVILLE	MARINE IM.	20	5	29.83	70.38	9.79
WAVERLY						
SUNBURY	SHALE AND SANDSTONE	655	10	0.00	0.00	100.00
BEREA						
BEDFORD						
DEVONIAN SYSTEM						
OHIO	SHALE	600	5	0.00	0.00	100.00
OLENTANGY	SHALE	20	2	0.00	1.00	99.00
DELAWARE	LIMESTONE	45	12	30.46	55.81	13.73
MARCELLUS	SHALE	10		0.00	1.00	99.00
COLUMBUS TOP	LIMESTONE	50	20	29.06	67.96	3.04
BOTTOM	DOLOMITE	40	24	84.72	11.69	3.59
LUCAS	DOLOMITE	50	6	86.30	9.50	4.20
AMHERSTBURG	DOLOMITE	15	1	83.23	14.23	2.54
ORISKANY	SANDSTONE	10				
SILURIAN SYSTEM						
MONROE	DOLOMITE	570	85	93.90	2.34	3.76
GUELPH-CEDARVILLE	DOLOMITE	170	64	98.02	0.20	1.78
SPRINGFIELD	DOLOMITE	20	21	84.80	3.13	12.47
EUPHEMIA	DOLOMITE	6	3	96.55	0.79	2.09
MASSIE	SHALE	5				
LAUREL	DOLOMITE	6	3	78.78	12.85	8.37
OSGOOD	SHALE	45				
DAYTON	DOLOMITE	8	5	70.01	17.20	12.79
BRASSFIELD	LIMESTONE	27	17	22.29	72.23	5.48
ELKHORN	SHALE	63	1	25.10	1.75	73.15
ORDOVICIAN SYSTEM						
RICHMOND	SHALE AND IM.	265	1	10.69	66.47	22.84
MAYSVILLE	SHALE AND IM.	205	4	4.33	47.88	47.78
EDEN	SHALE AND IM.	245	2	7.88	45.05	47.07
UTICA	SHALE	170	2	13.22	23.60	63.18
TRENTON	LIMESTONE	185	1	12.57	74.84	12.59
BLACK RIVER	LIMESTONE	425	2	14.14	79.83	6.03
GLENWOOD	SHALE AND DOLOMITE	10	1	22.99	4.04	72.97
LOWER MAGNESIAN	DOLOMITE	450		95.00	1.00	4.00
CAMBRIAN SYSTEM						
CAMBRIAN	DOLOMITE	715		54.49	0.81	44.70
CRYSTALLINE ROCKS						

LEGEND

DOLOMITE — SHALE & ETC.

LIMESTONE — CRYSTALLINE



LUCAS FORMATION

In Ohio the Lucas formation is local in distribution and is confined to an outcrop in western Lucas, northwestern Wood and southeastern Henry counties. The thickness is erratic, the maximum given being about 140 feet. The Lucas is characteristically a dolomite but locally becomes calcareous in composition.

The formation is rather definitely bedded, the layers commonly ranging from 3 to 12 inches in thickness. The stone varies from light bluish gray to light brown or drab in color. Disconformities exist both at the top and at the bottom of the formation but in any event the underlying and overlying strata are dolomites and not limestones. From 6 representative analyses the dolomite component, $CaMg(CO_3)_2$, varies from 53.68 to 97.93 per cent and averages 86.30 per cent. The limestone component, $CaCO_3$, ranges from 0.00 to 44.90 per cent but averages 9.50 per cent. The stone is moderately high in purity as the two carbonate components make up all but 4.20 per cent of the total. Both the geological and chemical data suggest that the Lucas formation was deposited under marine conditions with only slight local modifications from land influence.

AMHERSTBURG FORMATION

The lower formation, the Amherstburg, of the Detroit River group, in Ohio, is confined to two areas, one east of the Cincinnati arch in Ottawa, Erie and Sandusky counties and another west of this structure in Lucas, Wood and Henry counties. The rock is a dolomite in composition, slight drab to brownish gray in color, open or even cavernous in texture and usually massive in bedding. The thickness where best developed appears to vary between 50 to 75 feet. It is overlain mainly by the Lucas formation, a dolomite, and underlain by the Oriskany sandstone or by the disconformity marking this stratum. Commonly the underlying formation is the Monroe, strictly a dolomite in composition. The one analysis for the Amherstburg shows, dolomite, $CaMg(CO_3)_2$, 83.23 per cent, limestone, $CaCO_3$, 14.23 per cent and impurities 2.54 per cent. The lenticular and patchy nature of the deposits suggests marine origin with slight land influence.

MONROE FORMATION

The Monroe formation in Ohio includes the Greenfield, Tymochtee, Put-in-Bay and Raisin River divisions which, however, are not definitely separated one from another and are very similar in geological, physical and chemical features. Here these four members are treated as one formation. The thickness of these rocks varies from 400 to 700 feet and averages about 570 feet. They may present a shelly, very thin, thin, medium or massive structure. Such variations may be found in almost any quarry face or throughout any considerable part of the entire section. In general the materials are slightly siliceous in character, the free silica content being a rather distinguishing element. The color range is wide but in general the tints exhibited are some shades of brown or dark bluish gray. In texture the stone changes from hard and dense to open, sugary or even cavernous. Parts are very definitely laminated through the effects of thin papery partings of dark-colored matter which suggests the concentration of organic scums during dry land periods. Breccias, mud cracks and ripple marks are common impressions In the Monroe dolomites the fossils are not abundant, are small in size, and are usually preserved as casts. The anhydrite and gypsum deposits of central and northern Ohio and the salt beds, over 7,000 square miles, throughout the eastern part of the State are ordinarily present about midway in the section. The data are definite and conclusive and shows deposition in normal or even concentrated sea water under shallow water condition. During many times the basin became mud flats exposed to the sun. In no way is alteration, substitution or secondary changes

evident. The material was deposited as dolomite. The Monroe is overlain by the Oriskany sandstone or if this is not present by some dolomite formation, and underlain by the great Guelph-Cedarville dolomite also of high purity.

The Monroe formation in Ohio was thoroughly examined and sampled throughout its entire exposed range in the western part of the state. In an average of 85 samples the components are dolomite, $CaMg(CO_3)_2$, 93.90 per cent; limestone, $CaCO_3$, 2.34 per cent and impurities 3.76 per cent. In 42 of these samples the free limestone, $CaCO_3$, ranged from 0.00 to 0.10 per cent and in 24 others from 0.10 to 0.25 per cent. The only ones showing any considerable amounts of free limestone were in south-central Ohio abutting the area of overlap where the underlying Niagara limestone was a land surface through upper Silurian and lower Devonian time. Here in a small area the rock becomes a dolomitic limestone. Aside from this the Monroe conforms strictly to direct deposition as a dolomite, close to the true chemical ratio. It was laid down as a primary deposit in shallow marine waters, generally normal or above in saturation.

GUELPH-CEDARVILLE FORMATION

The Guelph-Cedarville formation of the Niagara group covers a wide area in Ohio. In southern and southwestern Ohio such rocks are exposed in sixteen counties and in the north-central part of the area in eight counties. The thickness varies from 80 to 200 feet. The rock is highly crystalline, usually open and porous in texture, nearly white, light gray or bluish gray in color and always of high purity. The formation is massive in structure, thick faces often showing few if any well-defined partings. In local areas some chert appears in the lower portion in 5 to 25 feet of strata. The rock is everywhere a true dolomite, at or very close to the dolomitic ratio. The Guelph-Cedarville formation is overlain by the Monroe dolomite and underlain by the Springfield-West Union dolomite, another division of the Niagara group. Throughout the area of outcrop the Guelph-Cedarville formation was carefully sampled for testing, in all 65 samples were taken and tested. The average of these show, dolomite, $CaMg(CO_3)_2$, 98.02 per cent; limestone $CaCO_3$, 0.20 per cent and impurities 1.78 per cent. Of these, 42 samples had a free limestone content, $CaCO_3$, of 0.10 per cent or less and only 6 had quantities above 0.50 per cent. In the true Guelph of northern Ohio the average content of silica, SiO_2, is about 0.16 per cent and that of alumina, Al_2O_3, is not more than 0.05 per cent. The minimum recorded is 0.05 SiO_2 and 0.02 Al_2O_3. In the Cedarville of southern Ohio these components average close to 0.54 SiO_2 and 0.13 Al_2O_3. Such contents of silty materials certainly show these seas had little contact with land areas. The Guelph-Cedarville formation is thus a dolomite of exceptionally high purity, with little or no free limestone, $CaCO_3$, and evidently deposited under true marine conditions.

SPRINGFIELD-WEST UNION FORMATION

A definite group of strata of lenticular character near the base of the Niagara series is termed the Springfield-West Union formation. These deposits outcrop over a rather wide area in southwestern Ohio, vary in thickness from 10 to 40 feet and in general are dolomites somewhat siliceous in composition. They are directly overlain by the great Guelph-Cedarville formation and underlain by a series of calcareous shales and thin dolomites. The formation was carefully sampled throughout the area. In 21 samples the average components are: dolomite, $CaMg(CO_3)_2$, 84.40 per cent; limestone, $CaCO_3$, 3.13 per cent and impurities 12.47 per cent. The free limestone, $CaCO_3$, varies from 0.10 to 18.14 per cent and commonly—in 14 of 21 samples—ranges between 1.00 and 5.00 per cent. These analyses thus show a tendency towards slight dilution of the sea water or influence from land areas.

EUPHEMIA FORMATION

The Euphemia formation is the basal portion or a lens-like stratum of the great mass of Niagara dolomites. The rock is massive, porous and more or less mottled and commonly rich in fossils, preserved mainly as casts. The formation is relatively thin, averaging only about 6 feet. The outcrop of the member is confined to five counties. Three samples show the following average components: dolomite, $CaMg(CO_3)_2$, 96.55 per cent; limestone, $CaCO_3$, 0.76 per cent and impurities 2.69 per cent. The range of free limestone, $CaCO_3$, is from 0.00 to 2.24 per cent. The deposits are thus of marine origin in sea water close to normal in concentration.

LAUREL FORMATION

The Laurel formation is a thin, rather local unit, bedded in the calcareous shales, underlying the great body of Niagara dolomite. It is directly overlain by the Massie shale and underlain by the Osgood shale, both of which are made up largely of much land derived sediments. The rock is finely crystalline, dense and hard, is bluish gray in color and somewhat fossiliferous. Three analyses, relatively representative, furnish the following data on components: dolomite, $CaMg(CO_3)_2$, 78.78 per cent, limestone 12.85 per cent, and impurities 8.37 per cent. Its interbedding in shales, free limestone and moderate impurities all indicate influence from fresh water from land areas.

DAYTON FORMATION

The basal formation of the Niagara group is the Dayton member. It is directly overlain by the Osgood shales and underlain, with a slight disconformity, by the Brassfield limestone. The deposits are thin, varying from 7 to 13 feet and averaging only about 8 feet. The stone is thin bedded, compact, tough, crystalline and fossiliferous. In composition it is commonly a siliceous, limy dolomite. The results of five determinations are as follows: dolomite, $CaMg(CO_3)_2$, 70.01 per cent; limestone, $CaCO_3$, 17.20 per cent and impurities 12.79 per cent. The variation in dolomite is from 68.14 to 73.21 per cent and in limestone from 15.40 to 20.01 per cent.

A study of the preceding formations shows an increase downward in the quantity of free limestone, $CaCO_3$, and in the quantity of shale sediments for example:

	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Impurities
Guelph-Cedarville formation	98.02	0.20	1.78
Springfield-West Union formation	84.40	3.13	12.47
Euphemia formation	96.55	0.76	2.69
Laurel formation	78.78	12.85	8.37
Dayton formation	70.01	17.20	12.79

Thus the shift is from dolomites towards limestones which are the predominating rocks in the great mass of shales several hundreds of feet in thickness in the basal portion of the Silurian and in the upper part of the Ordovician systems. Hence the shift is from normal marine waters toward that diluted by fresh water from the land surfaces.

BRASSFIELD FORMATION

The Brassfield limestone in the lower part of the Silurian system is, in a way, placed out in a shale section and is a dolomitic limestone of fair purity. It is underlain by the Elkhorn or Red Medina shale and this in turn by that shale-limestone series of the Cincinnati group, in all about 900 feet in thickness. The Brassfield formation thus shows the influence of land or fresh water conditions.

The Brassfield member is from 20 to 40 feet in thickness and averages about 30 feet. It varies laterally from massive strata to thin bedded layers with shale partings. In color it ranges from a very light gray, nearly white, through darker shades of gray, buff and pink to brownish red. Marine fossils are abundant, being most concentrated along the partings. In composition the formation gradates downward from a relatively pure limestone at the top to one decidedly dolomitic at the bottom. This relationship is shown below:

Sample Number	Thickness		$MgCO_3$	$CaCO_3$	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Impurities
	ft.	*in.*					
275	9	4	3.35	95.86	7.33	91.88	0.79
274	9	5	15.25	83.94	33.35	65.84	0.81
273	6	9	20.75	78.23	45.38	53.60	1.02

The average of 17 samples representing all parts of the formation along its entire outcrop in southwestern Ohio yields the following: dolomite component, $CaMg(CO_3)_2$, 22.29 per cent; limestone component, $CaCO_3$, 72.23 per cent and impurities 5.48 per cent. The range in dolomite, is from 3.30 to 81.85 per cent and in limestone, from 9.37 to 91.88 per cent. Thus during the deposition of the Brassfield formation the conditions were variable but always were more or less influenced by fresh water from the land areas.

ELKHORN OR RED MEDINA FORMATION

The Elkhorn shale of Ohio is the Red Medina of the driller and the Queenstown of the New York section. It is regional in distribution but variable in thickness. In Ohio, it ranges from 10 to 250 feet but averages not far from 60 feet. The Elkhorn member is a typical shale in character but locally contains sandy lenses and limy matter. The color of the drill cuttings is distinctive, being red or brownish red. In composition it is classed as a siliceous, dolomitic shale rich in potash K_2O, and in hematite, Fe_2O_3. The testing of one sample from an oil well gave the following results:

Sample Number	Thickness		$MgCO_3$	$CaCO_3$	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Impurities
	ft.	*in.*					
219	56	0	11.48	15.37	25.10	1.75	73.15

The analysis shows that the Elkhorn is a shale, argillaceous, ferruginous and siliceous from land derived components and dolomitic from marine components.

RICHMOND, MAYSVILLE AND EDEN FORMATION

The Richmond is the upper formation of the Cincinnati group of the Ordovician system and is closely similar in every respect to the underlying Maysville and Eden formations. All are made up of great series of shales and limestone laid down with little alteration of the physical conditions. They were deposited in marine water, most certainly modified as to concentration. Here shale and limestone are repeated in rapid succession through a great thickness, 700 feet, of strata.

The deposits of the three formations are made up of alternate layers of shale and limestone, generally sharply defined but rather uniformly spaced. The hard carbonate rocks form from 20 to 50 per cent of the whole. These limestone strata range from 1 inch or less to 10 inches in thickness and are interbedded with the

shale, always calcareous in nature. The shale partings are on the average somewhat thicker than the limestone layers. The compositions of these formations as shown by a few analyses are given below:

	Thickness, feet	$MgCO_3$	$CaCO_3$	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Impurities, Shale, etc.
Richmond						
Stone and shale	265	4.89	72.27	10.69	64.47	22.84
Maysville	205					
Stone		1.61	83.26	3.52	81.35	15.13
Shale		2.40	14.53	5.25	11.68	83.07
Stone		2.20	85.62	4.81	83.01	12.18
Shale		1.72	17.54	3.76	15.50	80.74
Eden	245					
Stone		2.32	82.26	5.07	79.51	15.42
Shale		4.89	16.39	10.69	10.59	78.72

In composition these limestones closely duplicate the marine limestone of the Pennsylvanian system or of the coal formations. The bases conform to land or fresh water origin where the $CaO > MgO$. The associated shales are slightly more dolomitic in character. This rapid succession of shale-limestone, shale-limestone, repeated hundreds of times may be accounted for by seasonal inundations from the land areas which thus brought in greater supplies of bases, $CaO > MgO$, at each particular time. In a way it is comparable to the conditions in the Pennsylvanian system where inundations of the coal swamps, with diluted marine waters, gave rise to limestones or fossiliferous calcareous shales. Every coal bed in the Pottsville series and most of them in the Allegheny and lower Conemaugh series are directly or closely overlain by a marine limestone or fossiliferous shale. The end results in both cases, Cincinnatian and Pennsylvanian, are closely alike.

UTICA FORMATION

In Ohio, as detected by the drill, this formation ranges from 25 to 400 feet in thickness but averages close to 300 feet. It consists of calcareous, carbonaceous shales and shaly limestone, the latter being most concentrated in the lower portion. In color the Utica is conspicuous, ranging from brown to black, quite similar to the Marcellus, Ohio and Sunbury shales. The composition is shown below:

Sample Number	Thickness in Feet	$MgCO_3$	$CaCO_3$	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Shale, etc.
216	310	4.47	21.75	9.77	16.45	73.78
217	16	7.63	39.80	16.68	30.75	52.57

The organic nature of the coloring pigment is shown by the presence, in sample No. 216, of 0.33 per cent hydrocarbons, C_nH_{2n+2}. Both the organic matter, the shale component and the composition show the influence of land masses.

TRENTON AND BLACK RIVER FORMATIONS

The Trenton and Black River formations, commonly designated Trenton by the driller, make up a thick mass of carbonate rocks, averaging over 600 feet in thickness, which extends regionally across the state. These rocks are dark gray to dark in color, generally fine and dense in texture and vary from dolomitic limestones to true dolomites in composition. Where tested in the southwestern and central parts of Ohio they are limestone but in the northwestern part, in the old

Lima oil field, they are open, porous dolomites. The three analyses following are from the limestone area.

Sample Number	Thickness in Feet	$MgCO_3$	$CaCO_3$	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Impurities
Trenton						
220	185	5.75	81.66	12.57	74.84	12.59
Black River						
221	149	6.57	85.76	14.37	77.96	7.67
222	272	6.36	89.26	13.91	81.71	4.38

The composition of the Trenton and Black River formations indicates that these rocks were laid down in the sea where the conditions of salinity shifted, commonly depositing dolomitic limestone but more locally yielding dolomite.

LOWER ORDOVICIAN AND CAMBRIAN SYSTEMS

In Ohio where tested by the drill the rocks from the St. Peter sandstone of the Ordovician system through the Cambrian to the crystalline rocks of pre-Cambrian age are essentially dolomites and sandstone, the latter bedded in the former. From one set of 76 rough analyses the composition may be approximated about as follows:

	Thickness in Feet	Dolomite $CaMg(CO_3)_2$	Limestone $CaCO_3$	Sand and Other Impurities
Ordovician System				
Lower Magnesian	450	95.00	1.00	4.00
Cambrian System				
Upper part	580	66.00	1.00	43.00
Dresbach	135	5.00	0.00	95.00
Total	715	54.49	0.81	44.70
Crystalline rocks.				

The composition thus indicates normal marine deposits where the bases stand $Na > Mg > Ca$ and the acids $Cl > SO_4CO_3$.

CONCLUSIONS

A summary of the results of the composition of the carbonate rocks in the entire section in Ohio from the crystalline rocks through the Cambrian, Ordovician, Silurian, Devonian, Mississippian, Pennsylvanian and Permian systems to the unconsolidated recent materials is as given below:

Geological System	Thickness of Rock Tested	Dolomite Component $CaMg(CO_3)_2$ in per cent	Limestone Component $CaCO_3$ in per cent	Shale and Other Impurities in per cent
Permian	9	3.44	88.63	7.93
Pennsylvanian	131½	12.08	65.81	22.11
Mississippian	20	19.83	70.38	9.79
Devonian	200	58.86	35.33	5.81
Silurian	870	86.98	4.26	8.76
Ordovician				
Upper	1,505	10.94	60.00	29.06
Lower	450	95.00	1.00	4.00
Cambrian	715	54.49	0.81	44.70
Total	3,900½	48.10	28.96	22.94

Thus in the 3,900 feet of tested carbonate materials in a total section of 6,796 feet the dolomite component, $CaMg(CO_3)_2$, stands in the ratio to the limestone component, $CaCO_3$, of 48.10 to 28.96 or approximately about 5 to 3. The data show that the Silurian, lower Ordovician and Cambrian carbonate rocks are nearly entirely true dolomites. In the Devonian system the quantity of dolomite much exceeds that of limestone. In all of these true marine conditions of deposition prevailed. However, in the Permian, Pennsylvanian, Mississippian and Upper Ordovician systems the quantity of limestone much exceeds that of dolomite. Here the shift of conditions is toward fresh water or land influences. True dolomites were deposited in great masses (shown by over 80 samples) but pure limestones do not occur at any place in the section. The evidence from Ohio is quite conclusive and supports the view that dolomites are the natural deposits of the ocean where the salinity of the water is about normal, that is, where the bases stand $Na > Mg > Ca$ and the acids stand $Cl > SO_4 CO_3$. On the other hand limestones are deposited when the sea waters are somewhat diluted by fresh water from land areas in which the reacting components are largely found in the ratio of bases $Ca > Mg > Na$ and of acids $CO_3 > SO_4 > Cl$ or are tending in that direction. Hence both dolomites and limestones are primary in origin and have not undergone any alteration, one to the other.